

# A Kinetic Model for Limit Phenomena Prediction Based on Bifurcation Analysis

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**A bifurcation analysis was employed to construct a compact kinetic model to predict limit flame phenomena in steady state perfectly stirred reactors (PSR), including ignition, extinction and onset of flame instabilities. The method is demonstrated with dimethyl ether (DME)/air mixtures that involve the negative temperature coefficient (NTC) chemistry and thus showing cool flames in PSR. A Bifurcation Index (BI) is defined to quantify the contribution of each reaction to the limit phenomena. Reactions with large BI are selected and tuned to obtain a kinetic model that can accurately reproduce the bifurcation states obtained by the full mechanism.**

## I. INTRODUCTION

Limit flame phenomena, such as ignition, extinction and onset of flame instabilities are important for combustion applications. In a steady state system, ignition and extinction were typically believed to be associated with the turning points on the  $S$ -curves<sup>[1]</sup>. Such limit phenomena are induced by the competition between finite rate chemistry and the mixing processes. Therefore, accurate prediction of the limit phenomena requires realistic chemistry that is typically nonlinear, stiff and large, and thus computational expensive<sup>[2]</sup>. In the present study, a method based on bifurcation analysis was developed to construct efficient kinetic models that can accurately mimic the detailed mechanisms to predict limit flame phenomena.

A turning point on canonical  $S$ -curves is associated with a singular Jacobian matrix<sup>[3]</sup>, where changes in flame stability can occur. However, with detailed chemical kinetics, such as that of dimethyl ether (DME), the  $S$ -curve can be complex and involve multiple criticalities<sup>[4]</sup>. Furthermore, it was found using flame stability analysis that extinction of DME/air flames in steady state PSR may occur prior to reaching the turning points primarily due to the competition between different reaction pathways<sup>[5]</sup>. In such cases flame stability analysis is needed to rigorously detect the limit phenomena rather than simply depending on the turning points on the  $S$ -curves. In a recent study on chemical explosive mode analysis (CEMA)<sup>[6]</sup>, it was further shown that the limit phenomena in PSR is primarily induced by the competition between chemical explosive modes (CEM) and the mixing processes. As such, the species and reactions controlling the CEM can be similar to those controlling the limit phenomena.

In the present study, the controlling reactions for the limit phenomena are identified using a bifurcation index, defined in analogous to the participation index (BI) in computational singular perturbation (CSP)<sup>[7]</sup> and CEMA. Important reactions are selected based on their BI values to form a compact skeletal mechanism. The A-factors of reaction with large BI values are tuned to obtain  $S$ -curves that are mostly identical to those by the detailed mechanism.

## II. METHODOLOGY

The governing equations of a homogeneous combustion system, e.g. an unsteady PSR, can be represented by a set of ordinary differential equation (ODE):

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}(\mathbf{y}) = \boldsymbol{\omega}(\mathbf{y}) + \mathbf{s}(\mathbf{y}), \quad (1)$$

where  $\mathbf{y}$  is the vector of dependent variables,  $\boldsymbol{\omega}$  is the chemical source term, and  $\mathbf{s}$  is the mixing term. The time evolution of a small perturbation,  $\delta\mathbf{y}$ , induced to the steady state solution can be approximated with the following linear ODE:

$$\frac{d\delta\mathbf{y}}{dt} \approx \mathbf{J}_{\mathbf{g}} \cdot \delta\mathbf{y}, \quad \delta\mathbf{y} = \delta\mathbf{y}_0 \text{ at } t=0, \quad (2)$$

where  $\mathbf{J}_{\mathbf{g}}$  is the Jacobian evaluated with the steady state solution  $\mathbf{y}_s$ . Note that  $\mathbf{J}_{\mathbf{g}}$  consists of two components, which are attributed to the chemical source term and the mixing term, respectively.

$$\mathbf{J}_{\mathbf{g}} = \frac{\partial \mathbf{g}}{\partial \mathbf{y}} = \mathbf{J}_{\boldsymbol{\omega}} + \mathbf{J}_{\mathbf{s}}, \quad \mathbf{J}_{\boldsymbol{\omega}} = \frac{\partial \boldsymbol{\omega}}{\partial \mathbf{y}}, \quad \mathbf{J}_{\mathbf{s}} = \frac{\partial \mathbf{s}}{\partial \mathbf{y}} \quad (3)$$

The eigenvalue  $\lambda_1$  of  $\mathbf{J}_{\mathbf{g}}$  with the largest real part determines the absolute stability of the system, and a bifurcation point with  $\text{Re}(\lambda_1) = 0$  separates a stable branch from an unstable branch on the  $S$ -curve, where “ $\text{Re}()$ ” denotes the real part of a complex number. Note that, the Jacobian  $\mathbf{J}_{\mathbf{g}}$  is singular at the turning points of an  $S$ -curve, i.e.  $\lambda_i = 0$ . The turning points nevertheless may not necessarily indicate changes in flame stability if  $i \neq 1$ . In such cases, ignition and extinction of the system may occur at Hopf bifurcation points located away from the turning points<sup>[5]</sup>.

At a bifurcation point, where  $\text{Re}(\lambda_1) = 0$ , the eigenvalue can be decomposed as

$$\text{Re}(\lambda_1) = \sum_{r=1}^{I+1} \text{Re}(\lambda_r) = 0, \lambda_r = \mathbf{b}_1 \cdot \mathbf{J}_r \cdot \mathbf{a}_1$$

$$\mathbf{J}_\omega = \sum_{r=1}^I \mathbf{J}_r, \mathbf{J}_s = \mathbf{J}_{I+1} \quad (4)$$

where  $\mathbf{J}_r$  is the contribution of the  $r^{\text{th}}$  reaction to the chemical Jacobian,  $I$  is the total number of reactions, and  $\mathbf{b}_1$  and  $\mathbf{a}_1$  are the left and right eigenvectors of  $\mathbf{J}_g$ , respectively, associated with  $\lambda_1$ . The bifurcation index (BI) of the  $r^{\text{th}}$  reaction is defined as

$$\text{BI}^r = \frac{\text{Re}(\lambda_r)}{\max_{r=1, I+1} |\text{Re}(\lambda_r)|} \quad (5)$$

The value of  $\text{BI}^r$  therefore indicates the normalized contribution from the  $r^{\text{th}}$  reaction or the mixing process to the zero-crossing of  $\text{Re}(\lambda_1)$  at a bifurcation point.

### III. RESULTS

Fig. 1 shows the temperature profile, i.e. the S-curve, for a rich DME/air mixture calculated with a detailed mechanism with 55 species and 290 reactions<sup>[8]</sup>. Three stable branches (solid lines), the strong flames branch, the cool flames branch, and the no-flame branch, respectively, were observed in the top-down order, with  $E_{2b}$ ,  $E_{1b}$ ,  $I_{2b}$ , and  $I_{1b}$  being the extinction of strong flames, extinction of cool flames, ignition of strong flames, and ignition of cool flames, respectively.

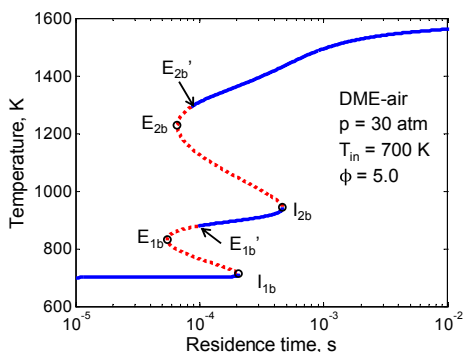


Fig. 1: An S-curve of a rich DME/air in PSR. Solid line:  $\text{Re}(\lambda_1) < 0$ , Dashed line:  $\text{Re}(\lambda_1) > 0$ .

The important reactions for the ignition and extinction states shown in Fig. 1 are identified using the BI values defined in Eq. (5), as shown in Fig. 2 for the extinction of the strong flames at  $E_{2b}'$ . A skeletal mechanism was formed by selecting the 103 reactions with non-negligible BI values ( $\text{BI} > 0.01$ ) from the detailed mechanism. The A-factors of a small group of reactions with large BI values at all the six bifurcation points in Fig. 1 are tuned such that the bifurcation points predicted by the tuned mechanism almost

exactly match those predicted by the detailed mechanism as shown in Fig. 3.

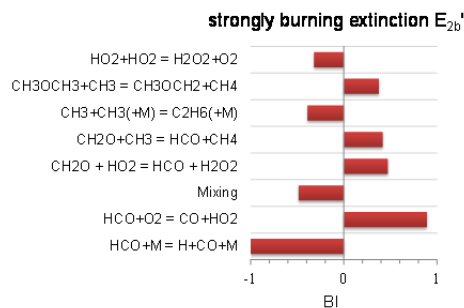


Fig. 2: Reactions with large BI values at strong flames extinction state,  $E_{2b}'$ .

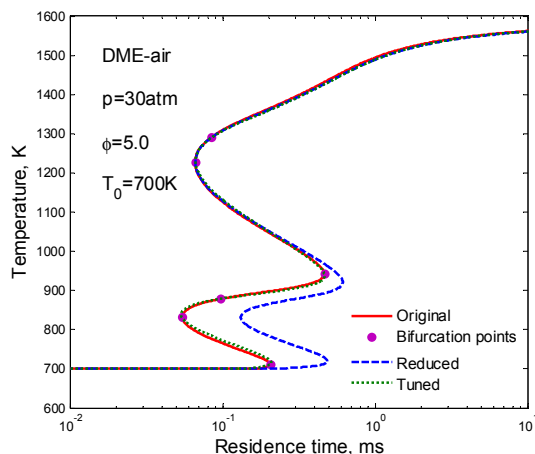


Fig. 3: The S-curves predicted by detailed, skeletal and tuned mechanisms for DME/air, respectively.

### ACKNOWLEDGMENT

This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, under Grant DE-SC0008622.

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